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THE REMOVAL OF MANGANESE (II) IN AQUEOUS SOLUTION BY USING REDUCED GRAPHENE OXIDE

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ABSTRACT

Due to growing population, new industries are being set up and the production is being increased with better quality products in the market using new technologies. But at the same time rising pollution causing concern specially for heavy metals. These heavy metals are discharged as effluents by industries like paint, tanneries, electronic devices, etc. Since rising concentration of heavy metals in nature is major cause of concern specially in our aquatic system like lake, river and ground water, there are available methods for removing these metals but they are costly. A Nano-material called Reduced Graphene Oxide had been assumed as a potential material to remove heavy metal at comparably better rate than existing process. Therefore the removal rate of heavy metal Manganese(II) at different quantity of absorbent has been tested with Reduced Graphene Oxide which has given some interesting results.

KEYWORDS: Heavy Metals, Water, Effluents, Manganese(II) & Reduced Graphene Oxide

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Original Article

INTRODUCTION

The most significant environmental problems that endangers the human beings throughout the world. The major environmental problem is of heavy metal pollution in our wastewater heavy metal ions such as As(III)/As(V), Pb(II), Cd(II), Ni(I), Cr(III)/Cr(VI), Zn(II), Cu(II), Hg(I)/Hg(II), Co(II) etc. containing wastewaters are directly or indirectly discharged into the streams, lakes, rivers or oceans increasingly, especially in developing countries it is due to rapid urbanization and industrialization such as metal plating, mining, tanneries, painting, batteries, paper industries, printing and photographic industries, pesticides and fertilizer industries, car radiator manufacturing, etc.[1]

Nausea, vomiting, diarrhea, asthma, pneumonia, skin degeneration, kidney and liver malfunction, congenital abnormalities, weight loss and various cancers can be the results of heavy metals found in industrial waste water when excessive exposure or intake of them can have dangerous consequences.[1]

Reduced Graphene Oxide is derived from Graphene Oxide in which both can be made through Modified Hummer's Method. Graphene is one of new material discovered by researcher from Manchester University in 2004 and won Noble Prize in Physics for their pioneering work in year 2010.[2]

It has large surface area and can be mix easily with water.

It is a single-atomic-layered material comprising carbon, hydrogen, and oxygen molecules by the oxidation of graphite crystals.[3].

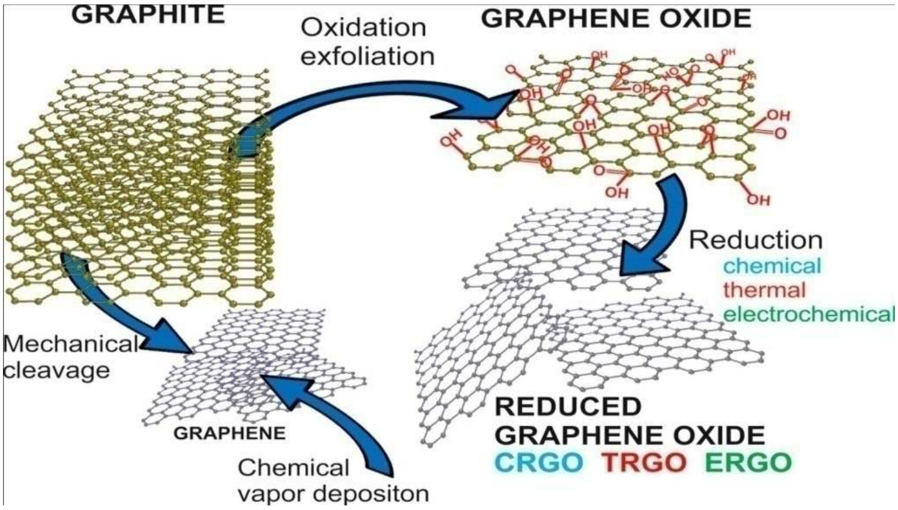

Figure 1: A Schematic Illustration of Possible Ways for Preparation of Graphene and rGO.[5].

Graphite is a three-dimensional (3D) carbon-based material consisting of millions of graphene layers, whereas graphite oxide is a little distinct. By oxidizing graphite with powerful oxidizing agents, oxygenated functionalities are implemented in the graphite framework, not only expanding the separation of the layer, but also making the material hydrophilic (that means they can be dispersed in water).A few techniques are feasible to convert graphite oxide into GO. Sonication, stirring, or a mixture of the two is the most popular methods. Sonication can be a very time-efficient way to exfoliate graphite oxide and is highly effective in exfoliating graphene; however, graphene flakes can also be severely damaged, reducing them to nanometers in surface size and producing a broad range of graphene platelet dimensions as well. The amount of layers is the major distinction between graphite oxide and GO. Although graphite oxide is a multilayer system in GO dispersion, it is possible to find a few layers of flakes and a single layer of flakes. [3]

Reducing GO to generater GO is an incredibly important method because it has a significant effect on the performance of the manufactured rGO; therefore, it will determine how near GO is to pure graphene in terms of composition (Chuang et al., 2014). In large-scale activities where scientists need to use big amounts of graphene for manufacturing purposes such as energy storage, rGO is the most evident option due to the comparative ease of generating adequate amounts of graphene with required performance concentrations. Although they are all techniques relying on chemical, heat, or electrochemical means, there is a range of ways to achieve decrease. Some of these methods can generate very high-quality rGO, comparable to pristine graphene, but can be complicated or time-consuming. [3]

There are some limits in the use in water treatment due to lack in dispersion because pure graphene is hydrophobic in nature. GO and rGO are effective in water purification due to the presence of surface functional groups. Negative surface charge of the GO and rGO helps efficient removal of cationic contaminants such as heavy metals. [4]

Characterization of Reduced Graphene Oxide (rGO)

The absorbent used in the removal of Manganese (II) is reduced graphene oxide (rGO); it has been procured from Platonic Nanotech Private Limited. All the reports whether it is characterization or the images of reduced graphene oxide used in this paper have been provided by the Platonic Nanotech Private Limited with written permission.

Characterization is a very important process as it tells the basic component of the material like composition of the elements, surface area, purity etc.

The table no. 1 tell us about the percentage of elements present in the given absorbent. It consists of Carbon, Oxygen, Hydrogen, Nitrogen and Sulfur. The table no. 2 tells us about the purity, thickness, surface area, etc.

FTIR means Fourier Transform Infrared Spectroscopy. It is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

FESEM is microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. It is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometer (= billion of a millimeter).

Table 1: Percentage of Elements Present in Reduced Graphene Oxide

Specifications	Atomic [%]
C	89%
O	9 %
H	2 %
N	0.04%
S	< 1%
(The table is taken from Characterization Report from Platonic Nanotech Private Limited with written permission)	

Table 2: Technical Data Values

Specifications	Value
Purity	99 %
Thickness	1–10 nm
Lateral Dimension	5–10 micron
Number of Layer	Average No. of Layer 4–8
Surface Area	210m^2/g
(The table is taken from Characterization Report from Platonic Nanotech Private Limited with written permission)	

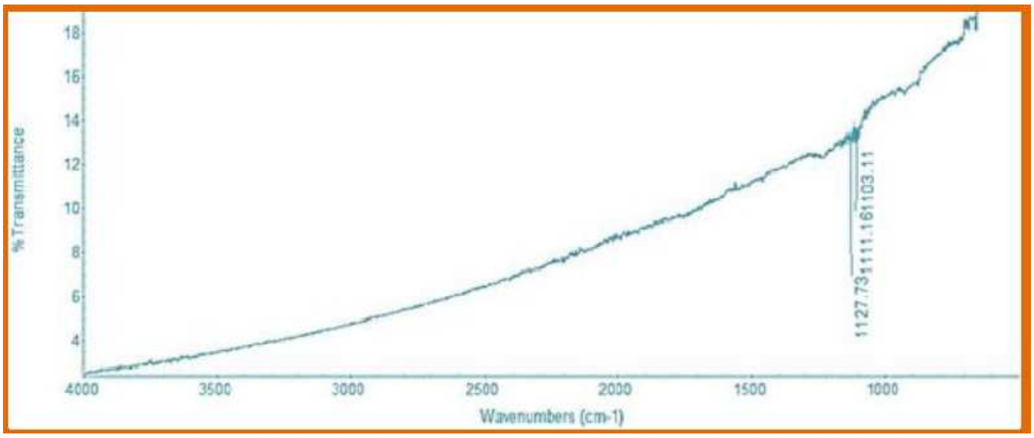

Figure 2: Image of FTIR Test Taken from Characterization Report from Platonic Nanotech Private Limited with Written Permission.

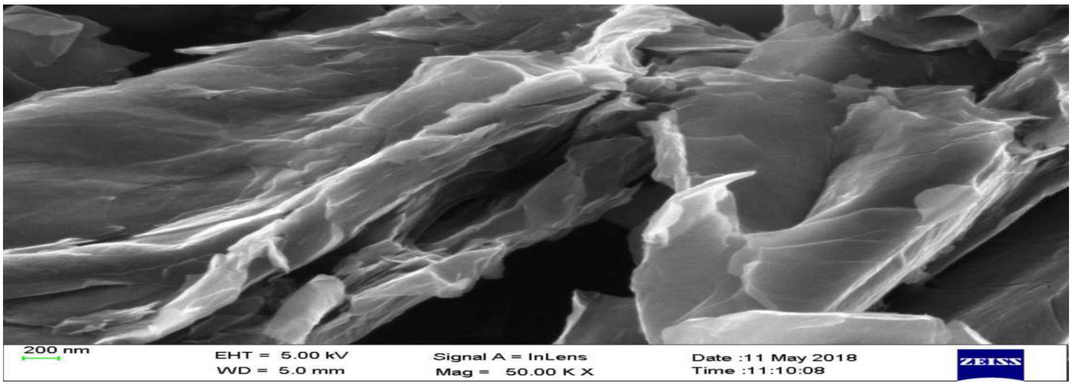

Figure 3: Image of FESEM (Field Emisson Scanning Electron Microscope) Test Taken from Characterization Report from Platonic Nanotech Private Limited with Written Permission.

How the Reduced Graphene Oxide is Different from the Graphene Oxide

There is no huge difference between the reduced Graphene Oxide and Graphene Oxide. But the main difference we can say is the purity. Both are made by the process of modified Hummer's method and when the Graphene Oxide is prepared then by the reduction method the reduced Graphene Oxide can be made. Reduction can be done in any of three ways like Chemical Reduction, Thermal reduction and UV light reduction. The reduction process is very complicated and critical, any mistake can reduce the purity, volume and other characteristics of the reduced graphene oxide.

The table no. 4 tells us about the purity, thickness, surface area, etc.

The difference can be seen clearly between the Graphene Oxide and Reduced Graphene Oxide, we can see clearly in the purity as the Graphene Oxide is less than 99% while in reduced Graphene Oxide is 99%. As we can see the thickness the Graphene Oxide is 1–5 nm but in reduced Graphene Oxide it is 1–10 nm**.**

But when we compare about the composition of elements the carbon content is less in Graphene Oxide as compared to Reduced Graphene Oxide.

And impurities are more in Graphene Oxide compared to Reduced Graphene Oxide.

Table 3: Percentage of Elements Present in Reduced Graphene Oxide

Element	Weight%	Atomic%
C	61.67	68.28
O	37.89	31.49
Na	0.27	0.16
S	0.18	0.07
(The table is taken from Characterization Report from Platonic Nanotech Private Limited with written permission)		

Table 4: Technical Data Values

Specifications	Value
Purity	>99 %
Thickness	1–5 nm
Lateral Dimension	5–10 micron
Number of Layer	Average No.of Layer 4–8
Surface Area	$210m^2/g$
(The table is taken from Characterization Report from Platonic Nanotech Private Limited with written permission)	

MATERIALS AND METHODS

Since the samples have to be experimented in the aqueous solution. That means all the solutions can be prepared and experimented in distilled water. The distilled water has been prepared in the lab (in figure no. 3) and the pH has been found to be 6.90, which is normal.

The samples are prepared as total 8 samples of Mn (II) of equal molarity i.e.0.0001 M. All are taken equally 8 samples of 50 ml. We have made 0.0001 M solution like we take one litre of distilled water and add 0.016901 gm of Manganese (II) Sulphate ($MnSO_4.H_2O$). The weight is taken after calculating all the molecular weight and the amount of solution which has to be made i.e. one litre solution. And we divide all eight samples into two parts. One part which is stirred for 30 min. with reduced graphene oxide and another part where sample is kept for 2 hours and stirred for few minutes. After stirring by using magnetic stirrer (figure no. 5), the samples are filtered with syringe filter or micro filter (figure no.6) with pore size 0.45 micron. Then the samples are tested in a device called as MP-AES.

The samples are tested for the pH of Mn (II) is 6.60 and for the distilled water which is discussed earlier is 6.90

Figure 4: The Distillation Apparatus.

Figure 5: Mn(II) Mixed with rGO.

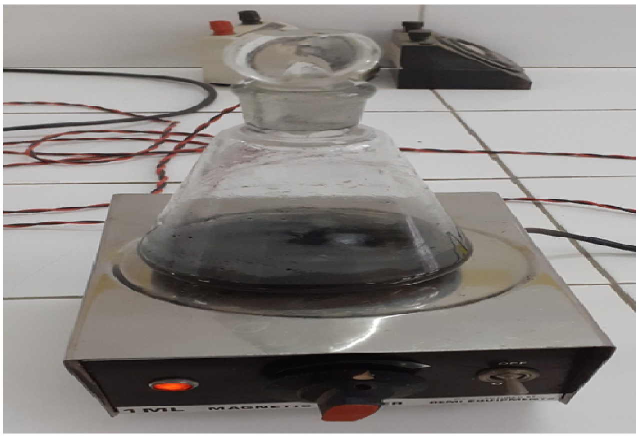

Figure 6: Magnetic Stirrer.

Figure 7: Micro Filter Attached with Syringe.

The micro filter or syringe filter plays an important role in the making of final samples. The micro filters used in the experiment process is of 0.45 microns. The main reason to use these micro filters is to remove the Nano- material i.e. Reduced Graphene Oxide (rGO). The main aim of removal of this rGO is

- To avoid any foreign particle (as Reduced Graphene Oxide) to choke or damage to the testing apparatus.
- To stop any further removal of the heavy metal from the adsorbent for the stipulated time as desired for experiment.
- The filter paper may not be so efficient and reliable as it may tear, choke at early process and even some fibers may come into the final sample they may possess danger to the testing equipment.

The samples are kept in very well washed bottles with distilled water and dried in clean environment.

RESULTS AND DISCUSSIONS

The preservation and analysis of the samples were done as per the Standard Methods (APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992).

The above results are in ppm and the ppm of manganese (II) is 16.901. That means the reduction rate of the manganese (II) comes in the range of 70%–78%.

Table 5: Weight of Absorbent and Final Concentration

Weight of Absorbent	30 Min.	2 Hour
0.0625gm	4.80 ppm	4.90 ppm
0.125gm	4.10 ppm	4.13 ppm
0.1875gm	4.02 ppm	4.06 ppm
0.250gm	4.00 ppm	4.01 ppm

The result shows as we increase the quantity of the absorbent i.e. Reduced Graphene Oxide the reduction rate increases but when the absorbent is added it must be continuously stirred before the filtration.

CONCLUSIONS

It has shown that the removal rate is near 78%. This conclusion can be:-

- The proper and continuous stirring of the sample is required and the absorbent is in sufficient quantity that there is no difference in time duration i.e. 30 minutes and 2 hours.
- The amount of reduced Graphene Oxide may be less than required as for that particular metal or for particular concentration of that metal to get better results.
- The pH of the water taken is more. As in other researches experimental researches the pH is preferred to be less than 4.5 for the best results.
- With proper and continuous stirring and keeping the same amount of reduced graphene oxide we may get the better results.

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